Supplementary material: Monitoring spin coherence of single nitrogen-vacancy centers in nanodiamonds during pH changes in aqueous buffer solutions

Masazumi Fujiwara,^{*,†,‡} Ryuta Tsukahara,[‡] Yoshihiko Sera,[‡] Hiroshi Yukawa,^{¶,§}

Yoshinobu Baba, \P, \S, \parallel, \perp Shinichi Shikata,[‡] and Hideki Hashimoto[‡]

†Department of Chemistry, Osaka City University, 3-3-138, Sugimoto, Sumiyoshi, Osaka 558-8585, Japan

‡School of Science and Technology, Kwansei Gakuin University, Sanda, Hyogo 669-1337, Japan

¶Department of Biomolecular Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

§Institute of Nano-Life-Systems, Institutes of Innovation for Future Society, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

||Health Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 2217-14, Hayashi-cho, Takamatsu 761-0395, Japan

⊥College of Pharmacy, Kaohsiung Medical University, Shin-Chuan 1st Rd., Kaohsiung, 807, Taiwan, R.O.C.

E-mail: masazumi@osaka-cu.ac.jp

1 Fluorescence saturation laser intensity

Figure S1 shows the dependence of the fluorescence intensity on the laser excitation intensity for single NV centers in 25-nm-sized nanodiamonds in water. The laser intensity used for the present spin measurements is indicated by the vertical dashed line at 0.25 mW. The solid line is the theoretical fit to the data based on the fluorescence saturation of two-level quantum systems.^{1,2} The saturation intensity is 0.34 mW.



Figure S1: The fluorescence intensity of single NV centers in water as a function of the laser excitation power. The saturation intensity is 0.34 mW. The gray shaded region is the power used for the spin measurements.

2 Zeta potential and its relationship to T_2

The pH is significantly related to the surface potential and, thus, would affect the electronic environment of the NV spins in nanodiamonds. The zeta potentials of the present sample give some information on the fluctuations. However, it is clear that it is difficult to measure the zeta potential of the nanodiamonds in the present experimental conditions because of the high ionic strength of the buffer solution. The present experiments use typical buffer solutions used in biochemical experiments (citric-acid–Na₂HPO₄ or Na₂CO₃–HCl) that stabilize the pH. In general, buffer solutions use weak acids and bases to stabilize the pH, and such weak acids/bases often have high ionic strengths. As seen in most colloidal solutions,^{3–6} a high ionic strength gives rise to aggregation/agglomeration and sedimentation of nanodiamonds.

Therefore, we had to reduce the ionic strength by diluting the buffer solutions by 20and 4-times for citric acid– Na_2HPO_4 and Na_2CO_3 –HCl, respectively. Figure S2 shows the dependence of the zeta potential of the nanodiamonds on pH in the diluted buffer solutions. As the pH increases (more basic), the zeta potential becomes more negative. This trend has been seen in oxidized nanodiamonds previously.⁷ On the basis of the zeta-potential data, we believe that the present nanodiamond samples basically have oxidized surfaces and that their optical and spin properties measured here reflect pH changes in the biochemical experiments realistically.

Note that the use of monoacids and monobases (such as HCl and NaOH) is a possible choice to enable both the zeta-potential measurements and the NV spin measurement under the same conditions.⁷ However, it is challenging to maintain the pH of strong acids/bases in the tiny chamber during the long period of the spin measurement, i.e., more than several hours. The difference of the ionic strength can also affect the NV spin properties. Rather using the mono-acids/bases, in this study, we stick to use the buffer solutions generally used in biochemical experiments. The present characterization of the NV spin properties could be used as a reference standard for future studies conducted in more biochemically (also biologically) realistic situations.



Figure S2: (a) Dynamic-light-scattering data of the nanodiamonds in water. (b) Zeta potential of the nanodiamonds as a function of pH. The pH range (4–7) was controlled by a citric acid–Na₂HPO₄ buffer solution and (8–10) by a Na₂CO₃–HCl solution. The solid line is a guide for the eye.

3 A NV-nanodiamond showing destabilization during the pH change



Figure S3: The dependence of T_2 (a) and ω_0 (b) on pH for a nanodiamond incorporating single NV center as an example of destabilization. The fitting error is increased in T_2 and ω_0 is shifted as pH changes from 7 to 11.

4 Fluorescence instability of NV nanodiamonds sometimes observed after the long photoexcitation



Figure S4: Time trace of the photon counts of the single NV fluorescence after the longterm laser excitation in buffer solution. The NV center was originally stable, but it was destabilized after several hours of green laser excitation. Strong fluorescent bursts were observed after long-term photoexcitation.

5 The dependence of the cw ODMR spectral shape and the spin properties on the number of data accumulation



Figure S5: (a) An ODMR spectra of the same single NV center acquired with different number of data accumulations from 20 to 320. (b) A plot of the peak positional determination precision (fitting error) as a function of the number of accumulation (measurement time). 20 accumulation takes about 120 s.

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